# White-Paper Recommendations For

## *Core Water Quality (Vital Signs) Monitoring Parameters for Marine and Coastal National Parks*

**Report of the National Park Service Vital Signs Monitoring Marine/Estuarine Workgroup**

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## Marine and Coastal Workgroup Participants

National Park Service
Roy Irwin, Senior Contaminants Specialist, Water Resources Division (Co-chair)
Charles Roman, Coastal Ecologist, CESU at University of Rhode Island (Co-chair)
Richard Curry, Science Coordinator, Biscayne National Park
Mietek Kolipinski, Aquatic Ecologist, Pacific West Region
John Portnoy, Ecologist, Cape Cod National Seashore
Lane Cameron, NPS, Santa Monica Mountains National Recreation Area (did not attend but participated in review process).

US Geological Survey
Hilary Neckles, Coastal Ecologist, USGS-Patuxent Wildlife Research Center

US Environmental Protection Agency
Donald Cobb, Atlantic Ecology Division, Narragansett
Walt Galloway, Atlantic Ecology Division, Narragansett
Gerald Pesch, Atlantic Ecology Division, Narragansett

State of Rhode Island
Christopher Deacutis, Environmental Scientist, RI Department of Environmental Management, Narragansett Bay Estuary Program

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## Introduction and Purpose

At the NPS-WRD sponsored workshop on water quality monitoring (November 2001), it was determined that workgroups should be convened to recommend a set of core water quality monitoring parameters for implementation at park units with freshwater and marine/estuarine resources. This report summarizes the deliberations of the marine/estuarine workgroup which met on April 3-4, 2002.

In addition to NPS scientists and managers from broad geographic regions and with varying water quality backgrounds, the marine/estuarine workgroup was fortunate to have representation from the USGS-BRD, US EPA, and state government. The EPA scientists were affiliated with EPA's National Coastal Assessment, a program that is implementing a suite of core indicators, in conjunction with states, throughout the coastal zone.

This summary report includes the following:

- Identification of core water quality monitoring parameters that could be collected, with identical methods, at all parks with marine/estuarine resources. A brief rationale is included for each selected parameter.
- Identification of and rationale for companion environmental parameters that are essential to collect in conjunction with the core water quality parameters.
- Identification of some optional water quality parameters that merit strong consideration for inclusion as core parameters at a subset of coastal/marine parks
- References Cited (all are available on the Internet, see references at end of this document).

It is noted that the workshop deliberations and this summary report merely focus on the identification of core parameters. Topics such as spatial and temporal sampling frequency, field methods, instrumentation needs, data analysis techniques, data management, and others, are all fundamental to implementation of a core water quality monitoring program, but were beyond the scope of this workgroup. However, on occasion we did discuss some of these topics and those discussions are reported here.

The parameters recommended by the marine/estuarine workgroup are fundamental to any long-term water quality monitoring program. As noted below, a long-term record of these basic parameters throughout the waters of marine/coastal parks will enable resource management professionals to detect trends related to global and regional climate change, as well as site-specific human-induced change. Moreover, a long-term data set of the selected fundamental parameters is essential to interpreting any trends noted from long-term biological and process-oriented data sets.

## Core Water Quality Parameters for Marine/Estuarine Waters

The charge of our workgroup was to select a few core parameters that could be applied to marine/estuarine sites on a Service-wide level to provide some capability of making statements regarding national trends in water quality. Water quality may be changing in response to site-specific human activities (e.g., watershed development, atmospheric deposition of pollutants), natural events (e.g., storms, altered geomorphology), and climate change. The selected parameters should allow investigators to address some of these general factors.

The following core water quality parameters were selected for monitoring within marine/estuarine waters of parks:

1) Water Temperature (degrees C°), rounded to nearest degree or to the nearest tenth of a degree if justified (see appendix for rounding rules)

2) Dissolved Oxygen (mg/L, ordinarily round to two significant figures, usually one whole number and one decimal place, unless otherwise justified)

3) pH (pH units, ordinarily round to nearest 0.1 units)

4) Ionic strength expressed as conductivity and as salinity. Salinity is a value calculated from conductivity, temperature, and if applicable, other factors such as depth or pressure. Unless otherwise justified, it is recommended that salinity should be calculated from conductivity using the equation from the Practical Salinity Scale of 1978 (see appendix). A calculator recommended for this conversation is the UNESCO/John Hopkins U. calculator (**http://ioc.unesco.org/oceanteacher/resourcekit/M3/Converters/SeaWaterEquationOfState/Sea%20Water%20Equation%20of%20State%20Calculator.htm**. Although other calculators are available, this one is recommended for the following reasons:

1) It appeared to be accurate and user friendly in some trials performed at Water Resources Division (Pete Penoyer, NPS, Personal Communication, 2003).
2) It is recommended by Frank Millero, University of Miami, RSMAS, an expert who has written on this subject extensively.
3) The calculator has some official status by being associated with UNESCO and John Hopkins University
4) The calculator allows one to enter either depth (zero at the surface) or pressure.

Can one simply read salinity from the meter? This is not recommended unless one has justified doing so by documenting that the meter is consistently calculating the right salinity to the nearest 0.1 unit. To make such a justification, one would typically have to

1. Minimize systematic error (bias) in the measurement of conductivity via calibration with high quality (preferably NIST) reference standards for conductivity,

2. Document that the answers the meter is providing for salinity are the same as the answers calculated from meter-provided conductivity values, using the UNESCO calculator (above).

Other recommendations related to salinity, conductivity, and specific conductance:

> Issues related to conductivity, specific conductance, salinity, and rounding rules can be complex. However, it is important that those monitoring the marine environment understand them, so some basics are discussed below and the reader can find more details in the appendix.
>
> In salinity trend work, one has to be careful that the measurement instruments, reference standards, and calculations used give consistent and comparable results. Do not attempt to detect trends in conductivity but instead
>
> Suggested rounding rules are given in the appendix (often not more than two or three significant figures are justified, often translating to no more than 0.1 decimal places).
>
> Specific Conductance (SC) may also be reported as an option if desired, but it is not required for marine or estuarine environments. SC final results should be given in mS/cm units for marine or estuarine systems.
>
> After reconsideration, the freshwater working group has also recently decided to require reporting conductivity: "WRD selected freshwater Specific Conductance (conductivity at 25º C) and marine Salinity (Practical Salinity Units at 15º C) for display and recording because these temperature compensated forms of conductivity offers field personnel the best direct and immediate comparison of this measurement with past data (i.e. with temperature effects removed to eliminate up to a 3% conductivity measurement change per degree C solely due to temperature). However, field probe measurements of Specific Conductance, Salinity and Total Dissolved Solids (TDS) are all "derived" measurements from (raw) conductivity meaning the instrument has a built-in algorithm in its software to automatically compute these "derived" parameters from conductivity. Not all manufacturers' instruments use the same built-in algorithm to obtain these "derived" values. For this reason, along with salinity, raw conductivity values should always be collected and reported.

Except for the recommendation that salinity should be calculated from conductivity rather than calculating specific conductance from conductivity, the four parameters are the same ones chosen by the freshwater working group (**http://www.nature.nps.gov/im/monitor/COREparam.doc**).

These four parameters represent our recommended essential minimum suite of parameters that should be included in a water quality monitoring. Many parks will and should augment these basic core parameters with additional ones with the objective of implementing a more comprehensive water quality monitoring program.

In what may be perceived as an irony by some, all 4 of these “required parameters” vary diurnally and often seasonally, particularly in estuarine sites, so trend detection is difficult unless one has high quality continuous monitoring data.

In trend detection, data comparability issues require especially strong scrutiny. For example, use of different meters or standard operating procedures (how long one lets a sample settle in the lab before taking a conductivity reading, for example) can cause changes in readings that might wrongly be attributed to trends.

Although trend detection may be complex, many would nevertheless argue that all four of the required parameters are needed for other reasons, including the fact that several of these are often needed as input data needed to calculate other values. Often the required parameters are also needed for site classification purposes.

**Other Associated Required Information:**

A) Location standard coordinates [for example, the Universal Transverse Mercator (UTM) grid; on USGS quad];
B) Local time (indicating standard or daylight-saving time);
C) Water depth and sample depth;
D) Tidal stage (e.g. high, low, or mid-tide) and direction (ebb, flood or slack water),
E) Estimated Wave Height.
F) Flushing time
G) Tidal range
H) Habitat description

In association with monitoring of the core water quality parameters, the following information should be collected in conjunction with the water quality collection. These data are important for interpreting any observed trends in water quality.

*Meteorological Data*

- Precipitation - ongoing and recent trends.
- Air temperature
- Wind speed and direction
- Barometric pressure

Suggested additional data for marine/estuarine sites included presence of shellfish, and external pathological condition of fish

As was the case in the freshwater working group, there was some discussion that the required parameters are so basic to the characterization of a waterbody, that their inclusion as “metadata” would be appropriate and would avoid the need for, or discussion of, a “required core parameter list” altogether. However, like the freshwater group, the marine/estuarine working group decided to avoid confusion, this approach should not be taken. Water column measurements do not fit the EPA definition of metadata ("data about data"). The conclusion reached by both the freshwater and marine workgroup was that requiring these parameters Servicewide is a reasonable approach, particularly given the need for a highly cooperative approach with other State and Federal organizations (where these parameters are routinely collected). Because most of these parameters are relatively easily obtained with multi-parameter probes (called "datasondes"), adding or deleting one or two parameters is not a significant cost or savings consideration, and therefore the exclusion of any single parameter makes little sense when synoptic sampling, if one or more of the other parameters are to be collected. For additional guidance on metadata, Data Reporting, and Archiving in STORET, see NPS Part E guidance at http://www.nature.nps.gov/im/monitor/wqPartE.doc.

### *Other Parameters Suggested For Consideration*

The marine/estuarine workgroup was charged with designing a simple, cost-effective water quality monitoring program. As stated, monitoring of water temperature, salinity, dissolved oxygen, pH, and required metadata represents a very basic water quality monitoring program. The workgroup did discuss some additional parameters that should be part of a water quality monitoring program if funds are available.

The following additional parameters are directly related to the issue of nutrient enrichment and contaminant loadings throughout the coastal zone. Although more comprehensive than the basic core parameters, these additional parameters remain quite fundamental to estuarine/marine monitoring;

- Fluorescence or chlorophyll *a*
- Submerged aquatic vegetation mapping
- Harmful algal bloom index
- Sediment Quality to include; organic content, grain size, contaminant levels
- Benthic species composition and abundance (the group strongly recommended that benthic macro-invertebrate samples be included at least once every five years, unless otherwise justified, using marine EMAP collection protocols).

Detailed discussions of other parameters of ten considered important:

> Nutrients: including total nitrogen (TN), total phosphorus (TP), nitrate, ammonia/ammonium, orthophosphate
>
> > Note: As pointed out in NPS Part B guidance: a typical older question to be answered, based on relatively simple limnology models was "How does anthropogenic nutrient enrichment cause change in the structure or function of near-shore coastal ecosystems?" As our model understandings have changed, numerous more detailed questions to be answered have evolved, such as "How does nutrient enrichment interact with other stressors (toxic contaminants, fishing harvest, aquaculture, non-indigenous

species, habitat loss, climate change, hydrologic manipulations) to change coastal ecosystems?" (J. E. Cloern, 2001, Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series 210: 223-253, **http://www.int-res.com/articles/meps/210/m210p223.pdf**).

Fecal Bacteria measures such as Enterococci bacteria, depending on what is currently recognized by and commonly monitored by the State.

Note: On July 21, 2003, the U.S. Environmental Protection Agency (EPA) published a rulemaking in the federal register that promulgated EPA's approval of test methods for the analysis of Escherichia coli (E. coli), Enterococci, Cryptosporidium and Giardia in fresh ambient water matrices. In addition, EPA approved test methods for the analysis of Enterococci in marine ambient water matrices (for details, see http://www.epa.gov/fedrgstr/EPA-WATER/2003/July/Day-21/).

Turbidity

Note: Two calibrated turbidity meters can give surprisingly different results on the same sample of water. The reason is that the meters are calibrated with a standard and very uniform suspension of particles. Natural water samples often do not contain a uniform concentration of particles. Because different turbidity meters have different geometries, the amount of scattered light detected by one meter can be quite different from another meter, even when they were both calibrated with the same standard. There is also something of an art to making the reading, because large particles can settle very rapidly. That is why some instead go with Secchi depths. The Secchi measurement seems crude, but the results are surprisingly (to me at least) consistent and operator insensitive (Ed Laws, University of HI, Personal Communication, 2003).

ASTM acknowledges rounding issues for turbidity. No more than two significant figures were recommended for results up to 1000 NTU units. Above 1000 NTU, up to 3 significant figures can sometimes be justified (ASTM. 1988. Standard Test Method for Turbidity in Water, D 1889-88A). However, measurement uncertainty is really a more complete way to express uncertainty in final results. See appendix for more general rounding rules discussions.

Secchi Disk and other water clarity measurements

Toxic contaminants such as PCBs and mercury in sediments and biota.

Normalization parameters helpful in the interpretation of the meaning contaminant concentrations. Like pH, such co-factors often drive toxicity,

> mobility, and bio-availability of the contaminants. In the water column, concentrations of sulfates and dissolved organic carbon are important in the probability of inorganic mercury being converted by bacteria to a more hazardous form, methyl mercury. In sediments, total organic carbon, sediment grain size, and sediment acid volatile sulfides are often important drivers of potential contaminant concentrations, mobility, and potential toxicity to biota. More information on these topics may be found in Part B Guidance for aquatic vital signs monitoring, available on the Internet (Irwin, 2003).

As with our recommended core parameters, the National Coastal Assessment includes water temperature, salinity, dissolved oxygen, and pH. However, additional water quality parameters are included (PAR, water column dissolved nutrients, chlorophyll *a*, and total suspended solids). Further, the National Coastal Assessment includes the following sediment and biological indicators: sediment contaminants, sediment toxicity, sediment characteristics, benthic species composition, fish community structure, contaminant levels in fish and shellfish, and external pathological condition of fish (Strobel and Heitmuller, 2001; Heitmuller, 2001; Bowman et al. 2000).

### *Photosynthetically Active Radiation (PAR)*

The work group initially recommended that light attenuation as measured by photosynthetically active radiation (PAR) be a required parameter. The group still strongly recommends that serious consideration be given to monitoring this parameter, especially in shallow environments where light penetration to the bottom is an important issue. However, there was more debate on PAR compared to the other candidate required parameters, due to difficulty with controlling the measurement for systematic error (bias) and issues with variability. These issues are summarized as follows.

> <u>Issues related to variability and representativeness</u>: In conducting research on processes affecting marine algae production in an aquaculture setting in Hawaii (the Big Island), I measured PAR at three treatments (surface, in air), subsurface (10 cm depth) and 30 cm deep in algae culture tanks (using LI-190SA, LI-192SA, and LI-193SA) quantum sensors connected to an LI-1000 data logger. A look at fifteen minute average values revealed that time of day, angle of the sun, cloud cover, airplanes flying over, etc. can influence even integrated values of PAR. Doing some type of comparative measure (surface and depth) might be reasonable, but I see so much potential for variation and expense in equipment acquisition and maintenance that some other measure of light attenuation, such as turbidity, might be less costly and less variable (Lane Cameron, NPS, Santa Monica Mountains National Recreation Area, Personal Communication, 2002).
>
> <u>Issues related to field calibration and control of systematic error</u>: It is impossible to take a high quality NIST standard into the field to see if the instrument can get a reasonably correct or expected answer. Therefore it is difficult to do a field check for systematic error (bias), or even a field calibration. EPA QA/QC

> guidance confirms that “No daily field calibration procedures are required for the LICOR light meter; however, the manufacturer recommends that the instrument be returned to the factory for annual calibration check and resetting of the calibration coefficient”( Heitmuller, 2001). Once a year calibration, though common place for this instrument, means that for long periods of time the instrument could be out of calibration and the user would not know it. If systematic error or even calibration cannot be checked in the field, some would argue that the measurement process is uncontrolled. If the measurement is uncontrolled, one cannot calculate measurement uncertainty and such data therefore lack optimal or defensible degree of quantitative credibility.

During the document review process, it was eventually decided to make PAR strongly recommended but not required at every site, due to

1. The expense of the instrument, and
2. Difficulties such as those outlined above, and
3. A less universal need to measure PAR in certain deep water oceanic environments.

When PAR is not to be measured, it is strongly recommended that either Secchi disk depth or turbidity be measured. The US EPA’s National Coastal Assessment is implementing, in cooperation with coastal states, a more comprehensive suite of core indicators that the NPS may want to consider as additional funds become available or implement within park waters in conjunction with the appropriate state agency that is involved with the National Coastal Assessment (Strobel and Heitmuller, 2001; Heitmuller, 2001; Bowman et al. 2000).

**Methods, Standard Operating Procedures, and QA/QC**:

The group recommended that marine/estuarine EMAP methods and QA/QC performance standards be adopted to ensure maximum data comparability with EPA and state data and to help ensure data credibility (Heitmuller, 2001).

All coastal States have standardized on EPA EMAP-Marine protocols; therefore, the group suggests that the EMAP National Coastal Assessment Field Operations Manual protocols (Strobel and Heitmuller. 2001) and QA/QC specifications (Heitmuller, 2001) be used for estuarine or marine areas whenever possible. EMAP QA/QC lists performance standards for the field measurement parameters. For example, the systematic error (bias) QC standards given for field probes, including water column data loggers, include the following:

> The measurement quality objectives (MQOs) for accuracy/bias (same as systematic error using NIST standardized terminology) for field measurements (including data logger/continuous monitoring units), based on comparison of the unit’s performance against reference standards or instruments, are:

Dissolved oxygen ± 0.5 mg/L
Salinity ± 1.0 ppt
pH ± 0.3 units
Temperature ± 1.0_ C
Depth ± 0.5 m (~ 2 ft)
Note from Roy Irwin: if calibration for pH is done with two standards as recommended by EPA, a third standard (NIST or other high quality standard) could be taken to the field for a final check of real-world systematic error/bias.
The precision repeatability MQO for all field parameters (including those listed above and Secchi depth and PAR) is a maximum allowable goal (presumably relative percent difference based on duplicate measures of the same sample) of 10% (Table A7-1 of the EPA QAPP at **http://www.epa.gov/emap/nca/html/docs/c2k_qapp.pdf**).

Some might react that these MQOs are not especially stringent, but the outdoor marine environment (bouncing around in boats, exposed to wind and sunlight etc.) is a difficult measurement environment, and the critical thing is that QC performance standards be stated, not that they necessarily be the world's most stringent. Measurement in the field is more difficult than in the lab, so the QC standards given are probably at least realistic. In fact, since it is hard to find comparably standardized QC performance standards for freshwater environments, and since probes in that environment often bounce around in pickups before being used, there was some discussion that the EMAP marine QC standards might even be considered as a default starting point for freshwater QC limits for field probe measures as well.

**Why Monitor These Parameters?**

The following discussion lists some of the benefits of monitoring the selected parameters, and includes some brief statements regarding sampling methods and frequency.

***Water temperature***

Why monitor ***water temperature***?

- Indicator of global climate change
- Controls biological species composition and abundance
- Determinant of primary and secondary productivity rates
- Regulatory role (i.e., thermal pollution)
- Contributes to oxygen demand in the aquatic environment
- Used to interpret trends in dissolved oxygen
- Used in calculations of toxicity of ammonia
- Relevant to water solubility of some contaminants, including some metals
- Water temperature is strongly correlated with and therefore a potential proxy for nutrient levels in many ocean systems
- Can be an indirect measure of habitat alterations (shallowness of water for example).

Suggested Instrumentation and Frequency: At minimum use instruments that can meet EMAP QA/QC performance standards. However, EMAP tends to require infrequent sampling. Since temperature is diurnally and seasonally variable, a continuous recording meter with data logger is suggested whenever possible, so that temporal variability can also be recorded. If continuous observations are not possible, sample at the same time of day or night, with minimum daily values expected at dawn and maximum values usually in mid-afternoon (e.g. 1400).

**Salinity, Calculated from Conductivity:**

Why monitor conductivity and calculate and report ***salinity***?

- Conductivity is needed to calculate salinity and specific conductance (SC). These are both estimates of ionic strength, with salinity more commonly reported in marine or estuarine systems and SC more commonly reported in freshwater systems.
- Salinity controls biological species composition and abundance
- Salinity is an indicators of trends in freshwater input to coastal waters
- Salinity is an indicator of water source to a waterbody (e.g., oceanic vs. freshwater)
- Salinity changes can be an indicator of global climate change
- Ionic strength controls mobility and speciation of metals and nutrients (e.g. $NH_4$) in the water column and sediments

Suggested Instrumentation and Frequency: At minimum use instruments that can meet EMAP QA/QC performance standards; however, EMAP tends to require infrequent sampling. This core parameter can be highly variable in estuarine/tidal areas, so a continuous recording meter with data logger is suggested so that temporal variability can also be recorded. Data comparability, trend, units used, and rounding issues are important and more complex than may be understood at first glance (see appendix for details).

***Dissolved Oxygen***:

Why monitor ***dissolved oxygen***?

- Controls biological species composition and abundance
- Except for anaerobic microbes, most living things cannot live without adequate concentrations of oxygen
- Hypoxia and anoxia indicate organic loading which can lead to eutrophication
- Indicator of water column primary productivity and respiration

- Indicator of water source (e.g., up welled water)
- Effects oxidation-reduction conditions, which in turn can effect pH balance and solubility and mobilization of metals and nutrients

Suggested Instrumentation and Frequency: At minimum use instruments that can meet EMAP QA/QC performance standards. However, EMAP tends to require infrequent sampling. Since DO is diurnally variable in many inshore habitats, a continuous recording meter with data logger is suggested as the optimal instrumentation, so that temporal variability can also be recorded. If continuous observations are not possible, sample at the same time of day or night, with minimum daily values expected at dawn (representing worst case conditions for aerobic biota) and maximum values usually in mid-afternoon (e.g. 1400) (best case).

Note from Lane Cameron:

> Relative to continuous measures of DO in marine or estuarine environments, membrane performance can degrade over time (sometimes very short periods of time, 24 to 48 hours) due to diatom fouling and other causes. Of all the continuous measurements that I took using YSI 6 Series data sondes DO was the most problematic showing a regular drop off with membrane fouling over relatively short periods of time. This process is highly variable and several of the newer instruments have automatic wiping mechanisms intended to deal with this. Additionally, current barometric pressure is used to calibrate the instruments that I have used and is entered into the logger at the beginning of the cycle and not changed or updated until a re-calibration event. If prolonged continuous measures are used the results are likely to degrade and measurement uncertainty is likely to increase (Lane Cameron, NPS Personal Communication, 2003). Note from Roy Irwin: all the more reason for checking precision repeatability and systematic error when the instrument is pulled out at the end of a monitoring period, and to consider correcting for data for drift.

***pH:***

Why monitor ***pH***?

- Controls biological species composition and abundance
- Controls solubility, mobility, degree of hazard, and speciation of metals and some other contaminants (such as ammonia).
- Indicator of water column primary productivity and respiration
- Indicator of global climate change

Suggested Instrumentation and Frequency: At minimum use instruments that can meet EMAP QA/QC performance standards. However, EMAP tends to require infrequent sampling. Since this core parameter can be quite variable in tidal and estuarine environments, a continuous recording meter should be used when practicable. A data logger is suggested so that temporal variability can be documented. If continuous observations are not possible, sample at the same time of day or night, with minimum daily values expected at dawn, due to respiration, and maximum values usually in mid-afternoon (e.g. 1400), due to photosynthetic uptake of dissolved $CO_2$, phosphate and nitrate.

***Light Attenuation:***

Why monitor ***light attenuation***?

- Controls rates of primary production and changes in species composition of primary producers (e.g., decreased light can lead to sea grass declines)
- Indicator of suspended sediment loading/runoff
- Indicates the effects of filter feeders in water clarity (high populations of filter feeders can increase water clarity).

Suggested Instrumentation and Frequency: Vertical light profiles using a meter (PAR, photosynthetically active radiation). Sample frequently during a summer index period that encompasses a 28-day astronomical period (i.e., full moon to full moon). The group suggests using both calibrated surface and depth sensors simultaneously.

Suggested alternative when PAR is not measured: Secchi Disc and/or Turbidity in NTU units. Secchi disc should be monitored when considerable comparable past data are available. Turbidity has the advantage of easier control of systematic measurement error and the advantage over Secchi of being available for continuous monitoring with data logger sondes (for details, see Irwin, R.J., 2004. Draft Part B of Aquatic Habitat Park Service guidance for Park Service Vital Signs Monitoring. Planning Process Steps: Issues To Consider And Then to Document In A Detailed Study Plan That Includes A Quality Assurance Project Plan (QAPP) And Monitoring "Protocols" (Standard Operating Procedures), Available on Internet at **http://www.nature.nps.gov/im/monitor/wqPartB.doc.**

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Heitmuller, T. 2001. National Coastal Assessment quality assurance project plan, 2001-2004. EPA/620/R-01/002. US Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL(**http://www.epa.gov/emap/nca/html/docs/c2k_qapp.pdf**)..

Irwin, R.J., 2004. Draft Part B of Aquatic Habitat Park Service guidance for Park Service Vital Signs Monitoring. Planning Process Steps: Issues To Consider And Then to Document In A Detailed Study Plan That Includes A Quality Assurance Project Plan (QAPP) And Monitoring "Protocols" (Standard Operating Procedures), Available on Internet at **http://www.nature.nps.gov/im/monitor/wqPartB.doc.**

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(**http://www.epa.gov/emap/nca/html/docs/c2kfm.pdf**).

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Gambrell, R.P. and W.H. Patrick 1980. Chemical availability of mercury, lead and zinc in Mobile Bay sediment suspensions as affected by pH and oxidation-reduction conditions. Amer Chem Society 14: 431.

Luther, G.W.I. and others 1991. Temporal and spatial variability of reduced sulfur species (FeS2, S2O3--) and porewater parameters in salt marsh sediments. Biogeochem. 14: 57-88.

Melville, M. and others 1999. Acid sulfate soils (ASS): Their impacts on water quality and estuarine aquatic organisms with special reference to East Australia and south China coasts. Asian Fisheries Science 12: 249-256.

Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 30: 147-201.

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**Appendix: Important Considerations and Definitions Related to Salinity and Conductivity**

## *General Guidance and Discussion*:

Special care should be taken when trying to determine whether or not there may be a trend related to conductivity, salinity, or specific conductance. Conductivity changes don't really mean anything unless temperature is taken into account. Changes in specific conductance and salinity changes may not be true changes unless only the same algorithms, calculations, and reference material standards were used. Meters that use different algorithms may not produce truly comparable results for salinity.

Because raw conductivity can change 3% with every degree change, one could observe drastically different conductivities between summer and winter, when the specific conductance value did not change. Also, if one rounds temperature to the nearest degree (on top of all this), one may be introducing additional error when calculating specific conductance from the raw data at a later date (Pete Penoyer, NPS, Personal Communication, 2003):

Partly to reduce these data comparability problems, unless otherwise justified, we recommend the use of the UNESCO/John Hopkins University calculator to derive salinity from conductivity and other factors (http://ioc.unesco.org/oceanteacher/resourcekit/M3/Converters/SeaWaterEquationOfState/Sea%20Water%20Equation%20of%20State%20Calculator.htm). As mentioned in the main body of this report, this calculator not only has some official status by being associated with UNESCO and John Hopkins University, but also is user friendly and allows one to enter either depth (including zero at the surface) or pressure. It performed well during WRD trials and is recommended by a well respected expert is also recommended by Frank Millero, University of Miami, an expert who also sent along the following helpful notes:

> The recommended practical salinity scale was defined in terms of the ratio of conductivity to KCl at 15oC. Oceanographers calibrate their salinometers using standard seawater that has a fixed conductivity ratio valid at 15oC. This reference has a salinity = 35.000 or near this value. The conductivity of seawater was determined by Alain Poisson as part of the UNESCO study 25 °C provided by Poisson [Poisson A. 1980. Conductivity/salinity/temperature relationship of diluted and concentrated standard seawater. IEEE Journal of Oceanic Engineering OE–5(1):41–50]. The equation is given in this paper and in my book F.J. Millero, 2001. The Physical Chemistry of Natural Waters, 2001 Wiley (http://www.wiley.com/WileyCDA/WileyTitle/productCd-0471362786.html). This equation should be used to determine the salinity from conductivity measurements. Most of the conductance bridges need to be calibrated at a few salinities (Frank Millero, University of Miami, RSMAS, Personal Communication, 2003).

Poisson also provided equations to convert specific conductance to salinity (http://www.iep.ca.gov/report/newsletter/2001winter/IEPNewsletterWinter2001.pdf).

Typically conductivity is measured and the instrument does the conversions to provide an (additional) readout of salinity. When salinity is reported for marine/estuarine waters, it should be reported as salinity in ppt (based on using the "Practical Salinity Scale of 1978" to convert conductivity to salinity) To further insure data comparability, systematic error (bias) and final calibration should be controlled by comparing results obtained with an International Organization of Standardization (ISO) reference standard. This distinction is made since various meter manufacturers algorithms to calculate to convert specific conductance or conductivity into salinity may not always produce consistent results. If ISO reference standards are used in calibration and in estimates of systematic error (bias), and if the meter used utilizes Practical Salinity Scale-consistent conversions, then salinity may be read from the meter. If not, salinity should be calculated from conductivity based on the Practical Salinity Scale of 1978,

Highlights of a helpful discussion on Salinity and the Practical Salinity Scale of 1978 from a Texas A. and M. website (http://www-ocean.tamu.edu/education/common/notes/chap6.html#6.1):

**Practical Salinity Scale of 1978** By the early 1970s, accurate conductivity meters could be deployed from ships to measure conductivity at depth. The need to reevaluate the salinity scale led the Joint Panel to recommend in 1978 that salinity be defined using only conductivity, breaking the link with chlorinity. The *Practical Salinity Scale of 1978* $S_{psu}$ in *practical salinity units* psu is now the official definition:

$$S_{psu} = 0.0080 - 0.1692K^{1/2}_{15} + 25.3851K_{15} + 14.0941K^{3/2}_{15} - 7.0261K^{2}_{15} + 2.7081K^{5/2}_{15} \quad (6.4a)$$

$$K_{15} = C(S,15,0)/C(KCl,15,0) \quad (6.4b)$$

$$2 \leq S \leq 42$$

where C(S, 15, 0) is the conductivity of the sample at 15° C and standard atmospheric pressure, and C(KCl, 15, 0) is the conductivity of the standard KCl solution at 15° C and standard atmospheric pressure; and where the standard KCl solution contains a mass of 32.4356 grams of KCl in a mass of 1.000 000 kg of solution.

**Comments** The various definitions of salinity work well because the ratios of the various ions in sea water is nearly independent of salinity and location in the ocean…Only very fresh waters, such as are found in estuaries, have significantly different ratios…because accurate measurements of chlorinity are more difficult to make in practice than are measurements of conductivity, salinity is now defined through conductivity (http://www-ocean.tamu.edu/education/common/notes/chap6.html#6.1):.

Other notes on Salinity:

The standard methods book (American Public Health Association, American Water Works Association, and Water Environment Federation. 1998. Standard methods for the examination of water and wastewater, 20th Ed. American Public Health Association, Washington, D.C) gives equations for calculating salinity from conductivity, including one that is valid for salinities of 0 to 40, and some other equations and suggested algorithms that are not obviously exactly the same as the equation on the Texas A. and M. website.

YSI uses and recommends Standard Methods (op cit, paragraph above), for the measurement of water and wastewater method #2520B for the calculation of Salinity (Rick Fielder, YSI, Personal Communication, 2003).

Although the UNESCO calculator is the one recommended herein, other calculators can be found. For example, one Internet calculator cites the Standard Methods equation and gives a calculator for surface waters only. The only inputs are conductivity and water temperature. This site states that equations used are based on the practical salinity scale and are valid for surface waters with salinity between 2 and 42 ppt. It further suggests consulting *Standard Methods for the Examination of Water and Wastewater* if users have questions or concerns (California volunteer monitoring group calculator on Internet at http://www.fivecreeks.org/monitor/sal.html, no government endorsement implied).

Oceanographic websites tend to produce calculators that can factor in pressure factors related to depth of the sample. For example (no government endorsement implied).

An Australian University has put calculators on the Internet (http://gaea.es.flinders.edu.au/~mattom/Utilities/) to calculate

Salinity from conductivity ratio, or,

Salinity from conductivity, temperature and pressure.

Similar calculators are found at http://www.oceantech.net/OceanographicCalculator.htm

Again, however, not all the calculators or all instruments appear to convert conductivity to salinity in ways that give identical answers, so for Park Service consistency and the reasons already detailed, unless other wise justified, we recommend the use the UNESCO calculator (http://ioc.unesco.org/oceanteacher/resourcekit/M3/Converters/SeaWaterEquationOfState/Sea%20Water%20Equation%20of%20State%20Calculator.htm.

The basis of the conversion is the conductivity ratio of a seawater sample and a standard KCl solution; by definition, a conductivity ratio of 1 yields a salinity of 35 on the practical salinity scale. In practice, all measurement devices are calibrated against a standard seawater. The method is not an "ISO" method per se. Instead salinity is calculated based on the Practical Salinity Scale of 1978, which defines salinity in terms of the ratio of the conductivity of a sample at 15C and 1 atmosphere to that of a standard KCl solution. That's where the "ISO" standard comes in -- the seawater standard is ISO approved (Hilary Neckles, USGS, Personal Communication, 2003).

## *Rounding Rules --How Many Significant Figures Should be Reported?*

Those reporting or archiving data (such as temperature, pH, and conductivity) that will commonly later be used in the calculation of another value, should be especially careful not to round so aggressively that they inadvertently contribute to cumulative rounding errors in later calculations. A typical example of historically taught rules of thumb is provided on a John Hopkins engineering school website (**http://www.apl.jhu.edu/Classes/Notes/Telford/SignificantDigits.pdf:**

1. In your calculations, use one or two extra digits in intermediate calculations to avoid round-off errors and then round off the final result appropriately.

2. What is appropriate rounding off of the final result?

   When performing additions and subtractions only, the final result may have no more significant digits after the decimal point than the number with the fewest significant digits after the decimal point.

   When performing multiplication and divisions only, the final result may have no more significant digits than the number with the fewest significant digits (ignore the decimal point).

Although rounding rules of thumb such as those quoted above have value, there is no single answer on the best way to determine the number of significant figures to use for all applications.

To some degree, many of the widely taught simplistic rounding rules reflected older (slide-rule era) thinking on how to at least crudely factor uncertainty into a final result. A community college website provides a plain language explanation of how rounding considerations relate to measurement precision and to uncertainty in final results:

> “A measurement reported as 45.67 mL indicates that the piece of equipment being used could be measured precisely to 0.1 mL and a reasonable guess can be made about the hundredths place. So, this measurement is taken as being somewhere between 45.66 and 45.68 mL. There is some uncertainty in that last decimal place, but since a reasonable estimate can be made for its value, the 7 is still significant.

> Using the same piece of equipment, it would be dishonest to report a measurement of 32.446 mL because the equipment can only measure out to ± 0.01 mL. Any decimal places beyond the hundredths place would be pure guesses, and not at all significant for the value of this measurement" (http://www2.aacc.cc.md.us/sciljtracey/CHE111/c111helpsigfig.htm)

With the advent of modern ways to express uncertainty and computers that will carry large numbers of "guard" digits to protect against cumulative rounding errors in subsequent calculations, we now have better ways to express uncertainty in final results. In the example given above, which takes into account only measurement precision, the value was rounded to 45.67. A more modern and more quantitative way to express uncertainty would be to use NIST measurement uncertainty calculations that take into account not only precision, but also other known contributors to uncertainty, such as measurement systematic error/ bias (N. Taylor and C. E. Kuyatt. 1994. Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results NIST Publication TN 1297 (http://physics.nist.gov/Document/tn1297.pdf). If one were using this method to express uncertainty in a final result rather than simply rounding a value to 45.67, one would instead calculate and express measurement uncertainty in the final result as an NIST measurement uncertainty plus or minus value to accompany the result. For example, if measurement precision was very good and the total measurement uncertainty was very low, such a result might be expressed as something like the following: 45.676 plus or minus the measurement uncertainty, perhaps something like 0.003. If the measurement uncertainty for a single measurement was very high (not so unusual in some environmental observations or measurements), the single point might be reported as something like 50 plus or minus 30. Uncertainty in a mean can be expressed in a properly framed confidence interval about the mean, lengthened by the amount measurement uncertainty about each data point.(for more details, see Park Service monitoring guidance at http://www.nature.nps.gov/im/monitor/wqPartB.doc.

Data reporters do not always know how the data they produce will be used in subsequent calculations. Data users perhaps need to pay even more attention to uncertainty and to rounding than data reporters. If one is trying to determine if there are trends or if one is trying to determine if one set of numbers is statistically different than another, one should typically use measurement uncertainty adjusted confidence intervals as discussed above.

A much more crude way and old fashioned way to account for uncertainty in a single data point, but probably better than not accounting for uncertainty at all, would be to use a rounding rule such as the one below, for final results based on factors such as measurement precision as reproducibility.:

> First determine the number of significant figures one could round the precision reproducibility values (repeat observations on the same substance by different persons or using different instruments) so that the rounded value reported would not change between observations. Next, add one to that number of significant figures, so that there is some uncertainty only in that last significant figure or

decimal place but so that the last significant figure is a reasonable estimate and not a pure guess.

It might be especially tempting to use a rounding rules based on precision only, such as the one above, to account for uncertainty in parameters that don't lend themselves to easy estimates of systematic error (bias), such as:

1. PAR
2. Bacterial Counts
3. Taxonomic Identification of Very Small Invertebrates or Other Difficult Taxa
4. Judgment Habitat Observations (Percent Embededness of Oysters)
5. Spike Recoveries of Chemicals in Difficult Matrices

In these types of parameters, the expected or correct answer is not always easy to identify, so systematic error (bias) is more difficult to estimate and it might be more tempting to confine uncertainty to precision (repeatability) aspects or even rounding rules only. However, even for these types of parameters, there is often some way to at least roughly estimate systematic error (bias). For example, sometimes the observation or estimate of an expert is considered "right" or "expected" result and the difference between that observation and those of rookies or trainees is considered systematic error (bias). In cases where one is not sure even an expert is "right", another approach would be to take the maximum difference (delta) between observations as systematic error (bias). In this case, the systematic error (bias) estimate would be the same as maximum difference in reproducibility (something, like the person doing it or the instrument changes) precision. That would then be the conservative (worst case) estimate of bias and the variance of that value would be added to the variance of the value for precision repeatability (nothing changes) in sum of squares NIST calculations of measurement uncertainty. This approach would perhaps overestimate systematic error (bias) and express it as a plus or minus factor, perhaps not a bad thing when the right answer is not easy to pin down. An approach such as this one would allow one to estimate NIST measurement uncertainty, and in most cases would still be superior to trying to use rounding rules as crude ways to account for uncertainty.

For those who wish to study rounding rules issues further, the plain language explanation and examples provided by John S. Denker (**http://www.av8n.com/physics/measurement-u.htm#bib-basic**) are recommended. These discussions:

1. Are well written,
2. Explain why there is no single best way to choose the number of significant figures justified,
3. Explain that NIST measurement is a better way to document uncertainty in the final result than rounding rules.
4. Explain how excess rounding can result in important cumulative rounding errors,
5. Explain how excess rounding can hinder picking signals out of noise, and

6. Provide spreadsheet examples relevant to signal to noise ratios. Signal to noise ratios are very relevant to detection limits, deciding when a stressor impact is causing a change considered beyond normal, and other important issues relevant to environmental monitoring.

In summary, there are hazards from excess rounding of intermediate values, and modern computers negate some of the reasons we previously had for doing so. The best way to express uncertainty in final results is by providing an NIST suggested calculation of measurement uncertainty. For those who are unwilling to take the time to do this, the alternative of rounding a final result single data point based on limits of precision repeatability, is perhaps better than nothing, and may be tempting for those parameters for which estimates of systematic error are difficult, but this option is almost always far less complete or quantitative than estimating total measurement uncertainty.

Finally, none of these considerations negates the need for data users to consider common sense rounding rules related to multiplication/division and adding and subtracting, such as those mentioned above.